COVER SHEET

A Raman spectroscopic study of the uranyl phosphate mineral bergenite

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Abstract

Raman spectroscopy at 298 and 77 K of bergenite has been used to characterise this uranyl phosphate mineral. Bands at 995, 971 and 961 cm^{-1} (298 K) and 1006, 996, 971, 960 and 948 cm^{-1} (77 K) are assigned to the ν_1 $(PO_4)^{3-}$ symmetric stretching vibration. Three bands at 1059, 1107 and 1152 cm^{-1} (298 K) and 1061, 1114 and 1164 cm^{-1} (77 K) are attributed to the the ν_3 $(PO_4)^{3-}$ antisymmetric stretching vibrations. Two bands at 810 and 798 cm^{-1} (298 K) and 812 and 800 cm^{-1} (77 K) are attributed to the ν_1 symmetric stretching vibration of the $(UO_2)^{2+}$ units. Bands at 860 cm^{-1} (298 K) and 866 cm^{-1} (77 K) are assigned to the ν_3 antisymmetric stretching vibrations of the $(UO_2)^{2+}$ units. U-O bond lengths in uranyls, calculated using the wavenumbers of the ν_1 and ν_3 $(UO_2)^{2+}$ vibrations with empirical relations by Bartlett and Cooney, are in agreement with the X-ray single crystal structure data. Bands at (444, 432, 408 cm^{-1}) (298 K), and (446, 434, 410 and 393 cm^{-1}) (77 K) are assigned to the split doubly degenerate ν_2 $(PO_4)^{3-}$ in-plane bending vibrations. The band at 547 cm^{-1} (298 K) and 549 cm^{-1} (77 K) are attributed to the ν_4 $(PO_4)^{3-}$ out-of-plane bending vibrations. Raman bands at 3607, 3459, 3295 and 2944 cm^{-1} are attributed to water stretching vibrations and enable the calculation of hydrogen bond distances of > 3.2, 2.847, 2.740 and 2.637 Å. These bands prove the presence of structurally nonequivalent hydrogen bonded water molecules in the structure of bergenite.

Key words: bergenite, parsonite, threadgoldite, phosphate, Raman spectroscopy, U-O bond length, uranyl

Introduction

Uranyl minerals exhibit considerable structural and chemical diversity, and reflect geochemical conditions dominant during their formation [1, 2]. The crystal structures of U^{6+} minerals, containing uranyl, $(UO_2)^{2+}$, in their crystal structures, are diverse owing to their unusual chemistries and to the unique nature of the coordination polyhedra about the U^{6+} cation [3]. Uranyl minerals as major constituents of the oxidized parts of uranium deposits are important from the environmental point of view [4]. Uranyl minerals are also important as phases formed during alteration (hydration-oxidation weathering) of spent nuclear fuel. Knowledge of uranyl phases is crucial to evaluate the long-term performance of spent nuclear fuel in a geological repository [5]. The paragenesis of many uranyl minerals can be

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understood in terms of local groundwater chemistry, the relative solubilities of minerals, and the stabilities of relevant solution complexes [6-8]

From the uranyl anion sheet topology point of view [3, 4, 9] four major structural classes of uranyl phosphate and arsenate minerals and their synthetic analogues have been recognized [10, 11]: (a) autunite and meta-autunite group, which includes minerals containing the autunite-type sheet in their structures; (b) phosphuranylite group, in which are included minerals containing the phosphuranylite-type sheet in their structures; (c) layered and framework uranyl phosphates and uranyl arsenates structures whose sheet-anion topology is identical to that found in uranophane; and (d) chain structures, i. e. structures based on infinite chains of uranyl polyhedra and either phosphate or arsenate tetrahedra. The phosphuranylite sheet contains uranyl pentagonal and hexagonal dipyramids that share edges to form chains that are cross-linked by sharing vertices and edges with phosphate and arsenate tetrahedra. In some cases, sheets in minerals of this group are linked by bonds to U^{6+} in the interlayer, resulting thus in framework structures [3, 4, 9, 10, 12].

Bergenite is one of a significant number of uranyl phosphates possessing the phosphuranylite anion sheet topology. This group consists of at least sixteen minerals [13], which include also phurcalite $Ca_2(UO_2)_3O_2(PO_4)_2.7H_2O$, dewindtite $Pb[H(UO_2)_3O_2(PO_4)_2].2\ H_2O$, dumontite $Pb_2[(UO_2)_3O_2(PO_4)_2].5\ H_2O$ phosphuranylite $(K,Ca)(H_3O^+)_3[(UO_2)_7(PO_4)_2O_4].8\ H_2O$ (and structurally related yingjiangite $(K_2,Ca)(H_3O^+)_3[(UO_2)_7(PO_4)_4(OH)_6].6\ H_2O$), phuralumite $Al_2[(UO_2)_3(PO_4)_2(OH)_6].10\ H_2O$, mundite $Al_2[(UO_2)_3(PO_4)_2(OH)_3].5.5\ H_2O$, vanmeersscheite, $U^{6+}[(UO_2)_3((OH)_2(PO_4)_2](OH)_4(H_2O)_4$, upalite, $Al[(UO_2)_3O(OH)(PO_4)_2](H_2O]_7$, and françoisite-(Nd), $(Nd,REE)[[UO_2)_3O(OH)(PO_4)_2](H_2O]_6$ with known crystal structures [1, 3, 10, 11].

The uranyl phosphate mineral bergenite of formula $[(Ba)_2(UO_2)_3(PO_4)_2(OH)_4.8H_2O]$ was first discovered in 1959 [13-15]. The type mineral originates from near Bergen, Saxony, Germany. Piret and Deliens [16] suggested that some cationic substitution occurs with calcium replacing barium in the structure and the formula of bergenite correspond to $Ba_{4/3}Ca_{2/3}(UO_2)_3(PO_4)_2(OH)_4.\sim5.5\ H_2O$. According to Locock and Burns [17] the crystal structure of bergenite is monoclinic with space group $P2_1/c$ and is of ideal formula $Ca_2Ba_4[(UO_2)_3O_2(PO_4)_2]_3(H_2O)_{16}$ [17]. A molecular model of bergenite based upon the structure as determined by Locock and Burns [17] is shown in Figure 1 [17]. Locock and Burns state that 'The uranyl pentagonal dipyramids share edges, forming dimers, which are linked to uranyl hexagonal dipyramids on either side, resulting in chains of dipyramids. Each uranyl hexagonal dipyramid shares two equatorial edges with phosphate tetrahedra, and the resulting uranyl phosphate chains are linked into sheets by the sharing of vertices of phosphate tetrahedra with uranyl pentagonal dipyramids of adjacent chains. The uranyl phosphate sheet in bergenite is a new geometrical isomer of the phosphuranylite group; the phosphate tetrahedra between the uranyl chains vary orientations in an up-up-down up-up-down (uuduud) pattern, and the pairs of tetrahedra attached to uranyl hexagonal dipyramids change orientations in a complementary same-same-opposite (SSO) manner (symbol

uuduudSSO)'. There are three symmetrically distinct U^{6+} in UO_2O_5 pentagonal dipyramidal polyhedra, two symmetrically distinct U^{6+} in UO_2O_6 hexagonal dipyramidal polyhedra, and three symmetrically distinct P^{5+} in PO_4 tetrahedra in the crystal structure of bergenite, and two formula units in its unit cell [10, 17].

Infrared spectroscopy and thermal analysis of the uranyl minerals inclusive of uranyl phosphate minerals was reviewed by Čejka [18]. Neither infrared nor Raman spectra of parsonsite are available. Only wavenumbers of the $(UO_2)^{2+}$ stretching vibrations, calculated force constant, and calculated U-O bond lengths were published [19]. Some Raman studies of uranyl phosphates have been undertaken [20-24]. The amount of published data on the Raman spectra of mineral phosphates is limited [25-29]. The Raman spectra of the hydrated or hydroxy phosphate minerals is severly limited. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1}, the antisymmetric stretching mode (ν_3) at 1017 cm^{-1}, the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 mode at 567 cm^{-1} [27, 28, 30]. S.D. Ross in Farmer (1974) (page 404) listed some well-known minerals containing phosphate which were either hydrated or hydroxylated or both [31]. The position of the phosphate bands for uranyl phosphates remains yet to be determined. The fact that the symmetric stretching mode is observed in the infrared spectra affirms a reduction in symmetry of the $(PO_4)^{2-}$ units.

As part of our on-going research into the use of Raman spectroscopy to assist in the elucidation of the structure especially of secondary minerals, including uranyl minerals, the Raman spectra of bergenite at 298 and 77 K are reported and related to the bergenite structure.

Experimental

The mineral bergenite

The mineral bergenite originated from Mechelgrun, Vogtland Mining District, Sachsen, Germany. Chemical analysis by an electron probe gave an analysis of UO_3 62.47%, P_2O_5 11.15 %, CaO 4.6 %, BaO 13.5%. These values are close to the theroertical values for a bergenite based upon the formula proposed by Locock and Burns [10, 11, 17].

Raman microprobe spectroscopy

Crystals of bergenite were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique.

It should be noted that because of the very small amount of sample supplied on loan from the museum, it was not possible to run the infrared spectra of some of the samples. This does show a major advantage of Raman spectroscopy in the study of uranium minerals is the ability to study very small amounts of mineral. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published elsewhere by the authors [32-38]

Results and discussion

From the crystal structure data by Locock and Burns [10, 11, 17] may be inferred that symmetry of the uranyls in pentagonal UO_2O_5 and hexagonal UO_2O_6 polyhedra and symmetry of the phosphate tetrahedra in the crystal structure of bergenite are lowered from $D_{\infty h}$ and Td, respectively. This is connected with splitting of doubly and triply degenerate stretching and bending vibrations and activation of vibrations in Raman and infrared spectra.

The Raman spectra of bergenite in the 900 to 1200 cm^{-1} region at 298 and 77 K are displayed in Figure 2. The results of the Raman spectral analysis and the suggested assignment of the bands are reported in Table 1. This spectral region is the region where the phosphate stretching modes and the antisymmetric stretching modes of the $(UO_2)^{2+}$ units are observed. There is a possibility of potential overlap of the the $(PO_4)^{3-}$ symmetric stretching bands and the antisymetric stretching modes of the $(UO_2)^{2+}$ units. Polarisation experiments show that the band at 995 (298 K) is significantly polarised and hence this band is assigned to the ν_1 $(PO_4)^{3-}$ symmetric stretching vibrations. It is noted that this band splits into two components at 77 K with bands observed at 1006 and 996 cm^{-1}. The structure of bergenite is complex with two formula units per unit cell with five structurally distinct U^{6+} and three structurally distinct P^{5+} [10, 17]. Thus several phosphate symmetric stretching vibrations may be forth coming. In this case bands at 995, 971 and 961 cm^{-1} bands (298 K) and at 1006, 996, 971, 960 and 948 cm^{-1} are assigned to the the ν_1 $(PO_4)^{3-}$ symmetric stretching vibrations. The band at 961 cm^{-1} is attributed to the ν_3 antisymmetric stretching vibration of the $(UO_2)^{2+}$ units. A low intensity band is observed at 948 cm^{-1} in the 298 K spectrum which shows increased intensity in the 77 K spectrum. This band might be the ν_3 antisymmetric stretching vibration of the $(UO_2)^{2+}$ units. The structure of bergerite is complex with 18 formula units per unit cell. Thus several phosphate symmetric stretching vibrations may be forth coming. In this case both the 995 and 961 cm^{-1} bands (298 K) are assigned to the the ν_1 $(PO_4)^{3-}$ symmetric stretching vibrations. The three bands at 1059, 1107 and 1152 cm^{-1} are attributed to the ν_3 $(PO_4)^{3-}$ antisymmetric stretching vibrations. The bands are observed at 1061, 1114 and 1164 cm^{-1} in the 77 K spectrum.

The Raman spectrum of bergerite between 700 and 900 cm^{-1} at both 298 and 77 K are shown in Figure 3. Two bands are observed at 810 and 798 cm^{-1} (298 K) and 812 and 800 cm^{-1} (77 K). These bands are attributed to the ν_1 symmetric stretching vibration of the $(UO_2)^{2+}$ units. The fact that two bands are observed is attributed to differences in the UO bond lengths of the $(UO_2)^{2+}$ units. U-O bond lengths in uranyls were calculated with an empirical relation by Bartlett and Cooney [39] $R_{U\text{-}O} = 106.5[\nu_1(UO_2)^{2+}]^{-2/3} + 0.575$ Å. Obtained results 1.801Å /810 cm^{-1} and 1.813 Å /798 cm^{-1} (298 K) and 1.799 Å / 812 cm^{-1} and 1.811 Å / 800 cm^{-1} (77 K) are

in agreement with the X-ray single crystal structure analysis of bergenite – on average 1.8015 Å [10, 17]. Bands at 860 cm^{-1} (298 K) and 866 cm^{-1} (77 K) may be attributed to the ν_1 $(UO_2)^{2+}$ antisymmetric stretching vibrations. Calculated U-O bond lengths in uranyl ($R_{U-O} = 91.41[\nu_3(UO_2)^{2+}]^{-2/3} + 0.804$ Å by Bartlett and Cooney 1989) 1.815 Å / 860 cm^{-1} (298 K) and 1.810 Å / 866 cm^{-1} (77 K) are also close to the X-ray single crystal structure data [10, 17]. Bands at 777 cm^{-1} (298 K) and 784 and 723 cm^{-1} (77 K) are attributed to the libration modes of water molecules.

The Raman spectra in the 100 to 600 cm^{-1} region are shown in Figure 4. It is clear that the spectra may be subdivided into two spectral regions namely 350 to 600 cm^{-1} and 100 to 300 cm^{-1}. The first region defines the phosphate bending modes and the second region the OUO bending and MO stretching and bending vibrations. Wavenumbers of the bands of the $(PO_4)^{3-}$ bending vibrations are located in the region 391-615 cm^{-1}. Bands at (444, 432, 408 cm^{-1}) (298 K), and (446, 434, 410 and 393 cm^{-1}) (77 K) are assigned to the split doubly degenerate ν_2 $(PO_4)^{3-}$ in-plane bending vibrations. The band at 547 cm^{-1} (298 K) and 549 cm^{-1} (77 K) are attributed to the ν_4 $(PO_4)^{3-}$ out-of-plane bending vibrations. There is an apparent slight shift to higher wavenumbers upon cooling to 77 K.

The spectral patterns in the 100 to 300 cm^{-1} are similar for the three samples analysed and at the two temperatures. Bands observed at lower wavenumbers than 300 cm^{-1} are assigned to the ν_2 (δ) $(UO_2)^{2+}$ and ν $(U\text{-}O_{ligand})$ and $\delta(U\text{-}O_{ligand})$ vibrations without any detailed attribution. Three bands are observed at 265, 205 and 145 cm^{-1} in the 298 K spectrum. The spectral profile between 200 and 300 cm^{-1} is better band separated in the 77 K spectrum. Bands are observed at 287, 271, 259, 248, 223, 207 and 149 cm^{-1} at 77 K. The intense band at ~145 cm^{-1} is ascribed to BaO vibrations. An additional band is observed at 136 cm^{-1}.

Water molecules and hydroxyls may play an important role in the crystal structure, its origin and stability of minerals during their formation and existence in nature [40, 41]. Bond-valence analysis for bergenite [10, 17] proves that only water molecules are present in the crystal structure of bergenite. The presence of hydroxyls in the bergenite formula, proposed by Bültemann and Moh [14] and later also by Piret and Deliens [42] and included in the mineralogical literature by Anthony et al. [13] and Mandarino and Back [43] does not agree with the bond-valence analysis [10, 17].

The Raman spectra of the 2800 to 3800 cm^{-1} region are shown in Figure 5. The spectral region is complex and shows the ν OH stretching vibrations of water molecules. In the 298 K spectrum bands are observed at 3607, 3459, 3295 and 2944 cm^{-1}. These four bands are assigned to the ν OH stretching vibrations of water molecules. The position of the bands is determined by the strength of the hydrogen bonds formed between the water and the uranyl and phosphate units. The strength of the hydrogen bonds is measured by the hydrogen bond length. The hydrogen bond lengths for the four bands at 3607, 3459, 3295 and 2944 cm^{-1} are > 3.2, 2.847, 2.740 and 2.637 Å [Libowitzky 1999] . These results are significant as it means that the water molecules in the structure are not equivalent. The stability of bergenite depends upon the water molecules. Better band separation is observed in the 77 K spectrum. The 3607 cm^{-1} band shifts to 3626 cm^{-1} at 77 K. This change signifies

a weakening of the hydrogen bond involving the H_2O units. Bands attributable to water OH stretching vibrations are observed also at 3545, 3484, 3441, 3375, 3273 and 2944 cm^{-1}. One possibility is that the increased number of bands is observed because the mineral undergoes a phase change. The 1200 to 1700 cm^{-1} region is shown in Figure 6. Two bands are observed in the 298 K spectrum in this spectral region at 1602 and 1330 cm^{-1}. The first broad band is attributed to the water bending vibration. The band at 1330 cm^{-1} may be probably assigned to the the OH deformation mode.

Conclusions

Raman spectra of bergenite measured at 298 and 77 K, are presented and interpreted with respect to the $(UO_2)^{2+}$ and $(PO_4)^{3-}$ stretching and bending vibrations. Number of bands attributed to these vibrations confirms the presence of structurally nonequivalent uranyl and phosphate units. U-O bond lengths in uranyls are calculated using the Bartlett and Cooney's empirical relations for wavenumbers of the ν_1 and ν_3 $(UO_2)^{2+}$. These values are in close agreement with those from the X-ray single crystal structure analysis of bergenite. Number and wavenumbers of the Raman bands assigned to the ν OH stretching vibrations support the conclusions of structure analysis that structurally nonequivalent hydrogen bonded water molecules are present in the structure of bergenite. O-H…O bond lengths are estimated and prove that a hydrogen bonding network in bergenite consists of very weak up to strong hydrogen bonds.

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References

[1]. P. C. Burns, Proc.Russ. Min. Soc. 132 (2003) 90.
[2]. P. C. Burns, Mat. Res. Soc. Symp. Proc. 802 (2004) DD3.2.1.
[3]. P. C. Burns, Rev. Min. 38 (1999) 23.
[4]. P. C. Burns, M. L. Miller and R. C. Ewing, Can. Min. 34 (1996) 845.
[5]. Y. Li, P. C. Burns and R. A. Gault, Can. Min. 38 (2000) 153.
[6]. F. C. Hawthorne, Geol.Ore Dep. 88 (2003) 45.
[7]. R. J. Finch and T. Murakami, Rev. Min. 38 (1999) 91.
[8]. T. Murakami, H. I. T. Ohnuki and T. Sato, Amer. Min. 82 (1997) 888.
[9]. P. C. Burns, R. C. Ewing and F. C. Hawthorne, Can. Min. 35 (1997) 1551.
[10]. A. J. Locock, PhD Thesis thesis, Notre Dame (Indiana, U. S. A.), **2004**.
[11]. A. J. Locock, P. C. Burns and T. M. Flynn, Amer. Min.t 90 (2005) 240.
[12]. P. C. Burns, Mat. Res. Soc.Symp. Proc. 802 (2004) 89.
[13]. J. W. Anthony, R. A. Bideaux, K. W. Bladh and M. C. Nichols, Handbook of mineralogy Vol.IV. Arsenates, Phosphates, Vanadates. - Mineral Data Publishing, Tucson, Arizona (2000).
[14]. H. W. Bultemann and G. H. Moh, Neues Jahr. Min. (1959) 232.
[15]. G. Wappler and G. Schubert, Berichte der Deutschen Gesellschaft fuer Geologische Wissenschaften, Reihe B: Mineralogie und Lagerstaettenforschung 14 (1969) 257.
[16]. P. Piret and M. Deliens, Bull.Min. 104 (1981) 16.
[17]. A. J. Locock and P. C. Burns, Can. Min. 41 (2003) 91.
[18]. J. Cejka, Rev. Min. 38 (1999) 521.
[19]. A. O. Matkovskii, S. V. Gevork'yan, A. S. Povarennykh, G. A. Sidorenko and A. N. Tarashchan, Min. Sbornik 33 (1979) 11.
[20]. R. L. Frost and M. Weier, Spectrochim. Acta A60 (2004) 2399.
[21]. R. L. Frost, Spectrochim. Acta 60A (2004) 1469.
[22]. R. L. Frost and K. L. Erickson, Spectrochim. Acta A 61A (2004) 45.
[23]. R. L. Frost and M. Weier, Neues Jahr. Min. (2004) 575.
[24]. R. L. Frost, J. Kristof, M. L. Weier, W. N. Martens and E. Horvath, J. Therm. Anal. Calor. 79 (2005) 721.
[25]. R. L. Frost, L. Duong and W. Martens, Neues Jahr. Min. (2003) 223.
[26]. R. L. Frost, W. Martens, P. A. Williams and J. T. Kloprogge, J. Ram. Spec. 34 (2003) 751.
[27]. R. L. Frost, W. Martens, P. A. Williams and J. T. Kloprogge, Min. Mag. 66 (2002) 1063.
[28]. R. L. Frost, P. A. Williams, W. Martens, J. T. Kloprogge and P. Leverett, J. Ram. Spec. 33 (2002) 260.
[29]. R. L. Frost, P. A. Williams, W. Martens and J. T. Kloprogge, J. Ram. Spec. 33 (2002) 752.
[30]. R. L. Frost, W. N. Martens, T. Kloprogge and P. A. Williams, Neues Jahr. Min. (2002) 481.
[31]. V. C. Farmer, *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*, 1974.
[32]. R. L. Frost, K. L. Erickson, J. Cejka and B. J. Reddy, Spectrochim. Acta A61 (2005) 2702.

[33]. R. L. Frost, K. L. Erickson, M. L. Weier and O. Carmody, Spectrochim. Acta 61A (2005) 829.
[34]. R. L. Frost, K. L. Erickson, M. L. Weier, O. Carmody and J. Cejka, J. Mol. Struc. 737 (2005) 173.
[35]. R. L. Frost, M. L. Weier, T. Bostrom, J. Cejka and W. Martens, Neues Jahr. Min. 181 (2005) 271.
[36]. R. L. Frost, R.-A. Wills, M. L. Weier and W. Martens, J. Ram. Spec. 36 (2005) 435.
[37]. R. L. Frost, O. Carmody, K. L. Erickson, M. L. Weier and J. Cejka, J. Mol. Struc. 703 (2004) 47.
[38]. R. L. Frost, O. Carmody, K. L. Erickson, M. L. Weier, D. O. Henry and J. Cejka, J. Mol.Struc. 733 (2004) 203.
[39]. J. R. Bartlett and R. P. Cooney, J. Mol. Struc. 193 (1989) 295.
[40]. F. C. Hawthorne, Z. Kristall. 201 (1992) 183.
[41]. F. C. Hawthorne, Geol.Ore Dep. 45 (2003) 100.
[42]. P. Piret and M. Deliens, Bull. Min. 104 (1981) 16.
[43]. J. A. Mandarino and M. E. Back, *Fleischer's Glossary of Mineral Species*, The Mineralogical Record Inc, Tucson, Arizona, U. S. A., 2004.

Bergenite				Suggested Assignment
298K		77K		
Centre	FWHM	Centre	FWHM	
3607	34	3626	14	OH stretching
		3545	18	“
		3484	37	“
3459	179	3441	51	“
		3375	75	“
3295	283	3273	91	“
2944	166			
1602	82	1610	43	Water bending
1330	68			Uranyl-OH deformation
1152	24	1164	13	Phosphate antisymmetric stretching
1107	20	1114	9	“
1059	18	1061	11	“
995	12	1006	9	Phosphate symmetric stretching
991	62	996	11	Phosphate symmetric stretching
971	7	971	13	“
961	12	960	8	$(UO_2)_{2+}$ antisymmetric stretching
		948	9	“
860	32	866	21	Water libration
810	13	812	11	$(UO_2)_{2+}$ symmetric stretching
798	18	800	11	$(UO_2)_{2+}$ symmetric stretching
777	89	784	36	Water librations modes
		723	38	“
592	22			$(PO_4)^{3-}$ ν_4 bending
547	34	549	29	“
515	80			“
444	23	446	17	$(PO_4)^{3-}$ ν_2 bending
432	20	434	14	“
408	18	410	12	“
396	44	393	21	“
391	9			
		287	12	
270	9	271	12	$(UO_2)^{2+}$ bending

265	48	258	9	„
256	9	248	29	“
224	26	222	12	“
205	30	207	12	Lattice modes
178	37	186	20	“
145	28	149	24	“
133	7	136	7	“
111	14	110	10	“

Table 1 Results of the Raman spectra of bergenite at 298 and 77 K.

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Figure 3 Raman spectra of bergenite between 298 and 77 K between 700 and 900 cm^{-1}.

Figure 4 Raman spectra of bergenite between 298 and 77 K between 100 and 600 cm^{-1}.

Figure 5 Raman spectra of bergenite between 298 and 77 K between 2800 and 3800 cm^{-1}.

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Table 1 Results of the Raman spectra of bergenite at 298 and 77 K.

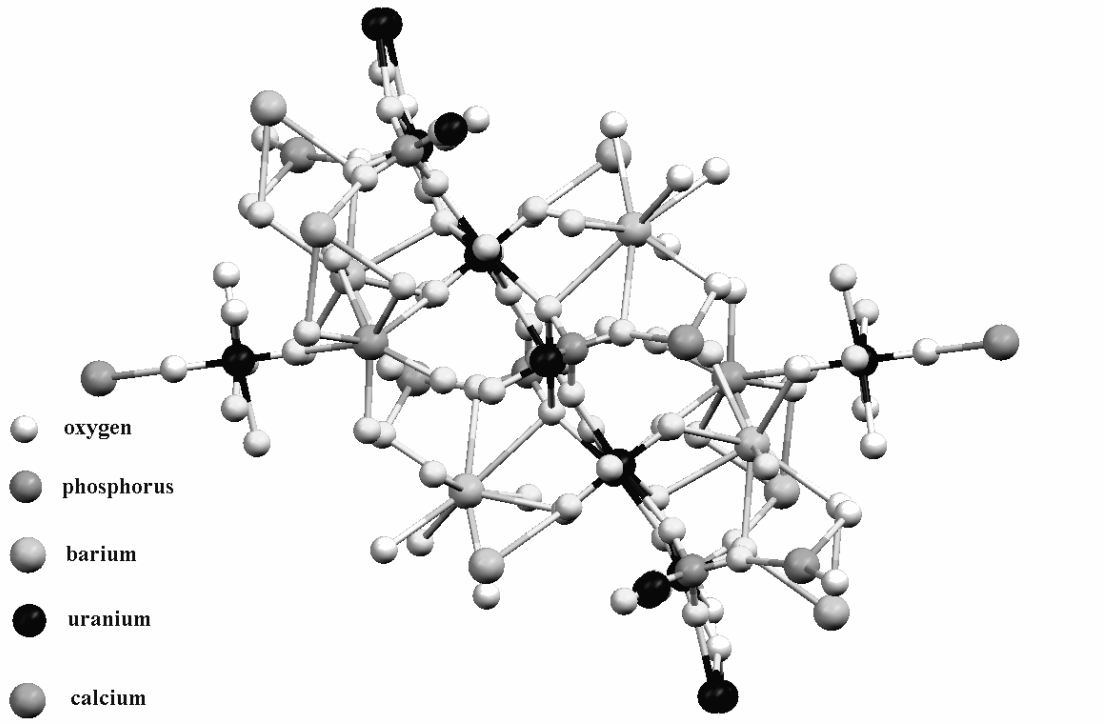

Figure 1

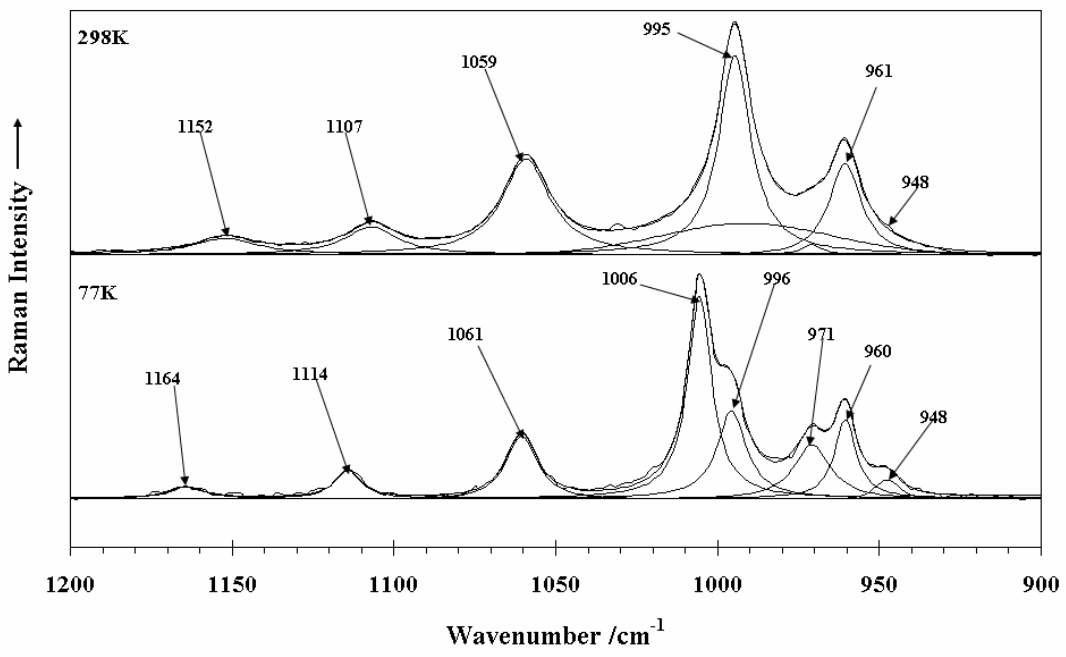

Figure 2

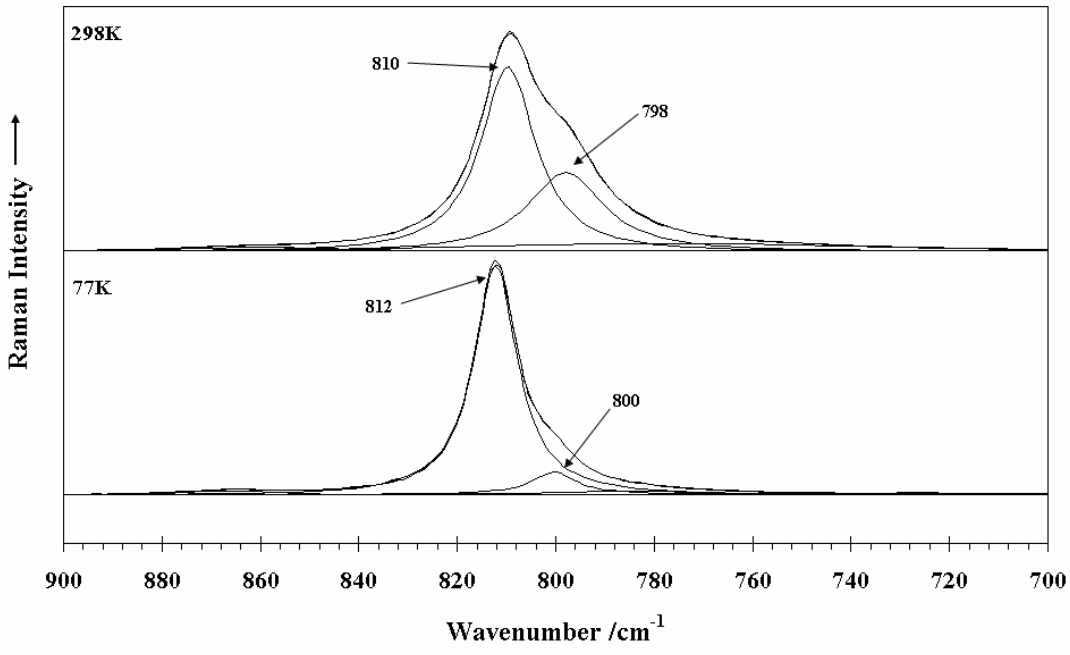

Figure 3

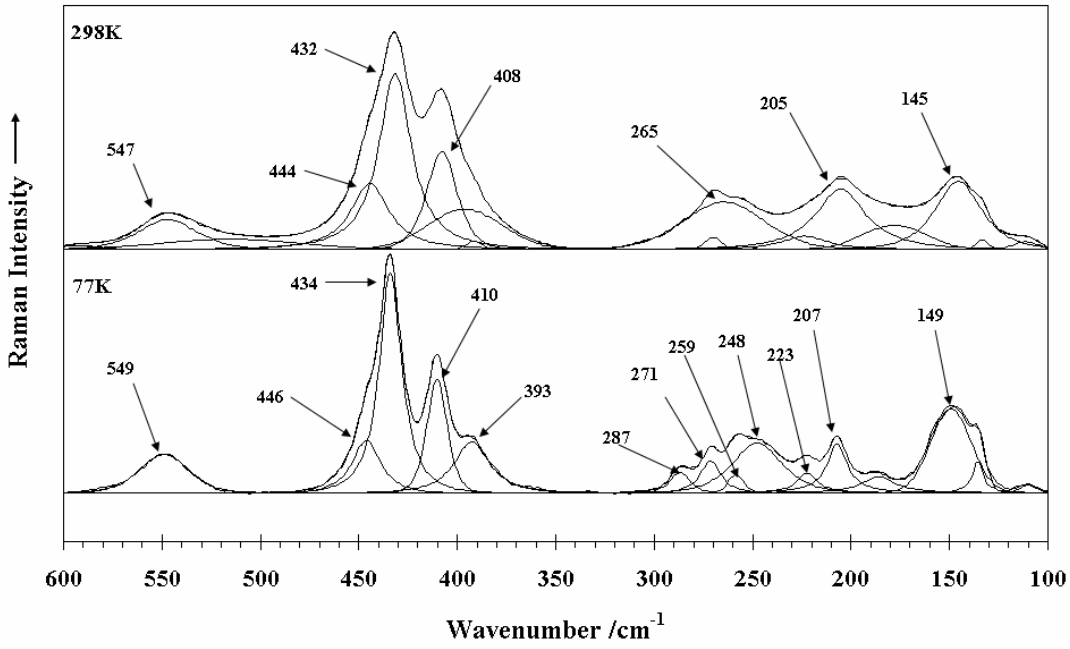

Figure 4

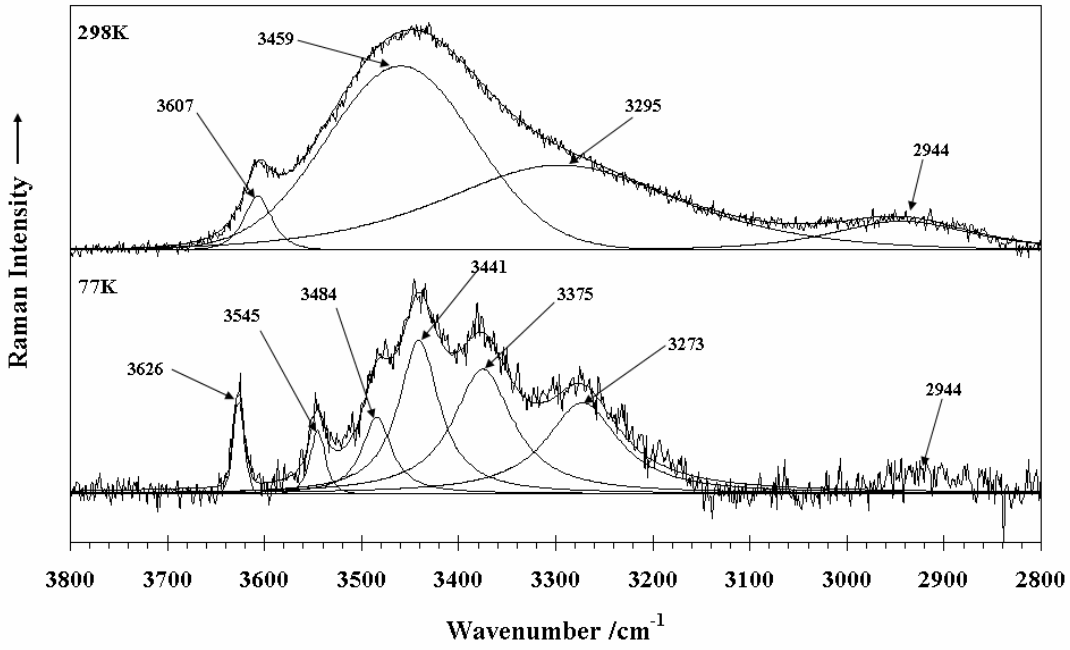

Figure 5

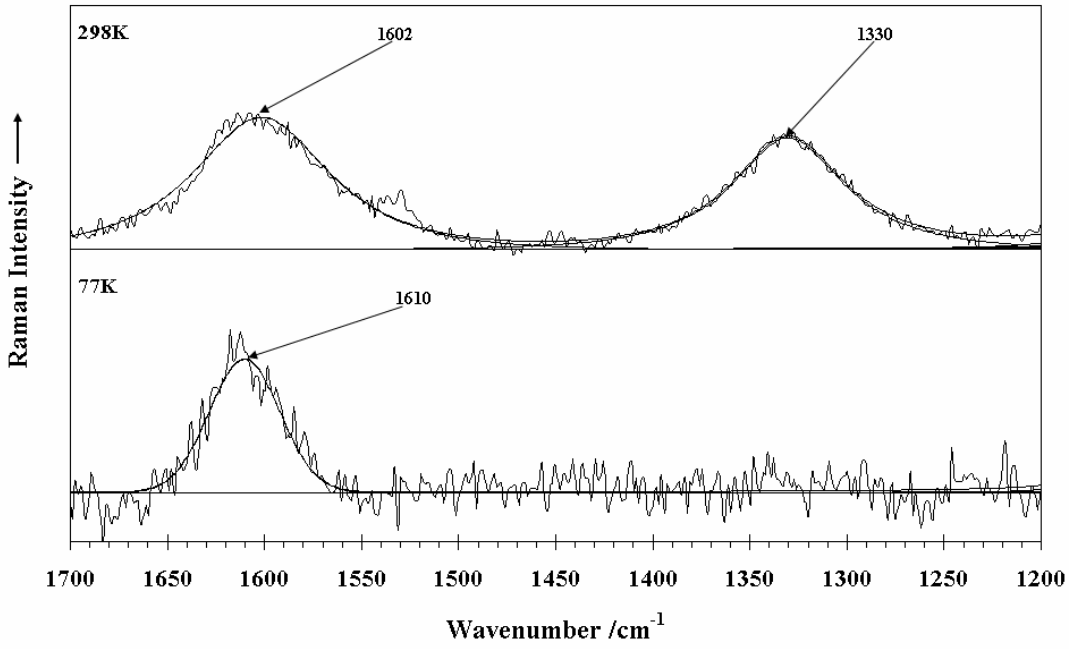
298K
1602
1330
77K
1610
Raman Intensity
1700
1650
1600
1550
1500
1450
1400
1350
1300
1250
1200
Wavenumber /cm-1

Figure 6